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E' Centers in Amorphous SiO_2 Revisited: A New Look at an Old Problem

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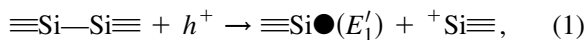
We present theoretical evidence that the paramagnetic E' defect centers in amorphous silicon dioxide ($a\text{-SiO}_2$) do not have the same microscopic structures as those well-defined in the corresponding crystalline counterparts such as α -quartz. We then present alternative models of some paramagnetic defects that account for the underlying experimental features of the E' -center variants in $a\text{-SiO}_2$. We suggest that our new model should take the place of the conventional defect model of $a\text{-SiO}_2$.

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Amorphous SiO_2 ($a\text{-SiO}_2$) is a material that is employed in diverse applications ranging from glass to catalysis to microelectronic devices and optical fiber waveguides [1,2]. Consequently, considerable efforts have been made in the past decades for a better understanding of the structure and properties of $a\text{-SiO}_2$. Although $a\text{-SiO}_2$ can be viewed as a conventional amorphous solid consisting of SiO_4 tetrahedra, there exist local configurations that are different from the average tetrahedral coordination geometry. These configurations are commonly called "point defects" by analogy with those in crystals, and the point defects in $a\text{-SiO}_2$ have been widely investigated for their role in modifying the electrical and optical characteristics of the silica-based materials [1–3].

The best known and examined point defect in silica (both in amorphous and crystalline forms) is the paramagnetic defect called the E' center [4]. The E' center can be regarded as a neutral silicon atom bonded to three oxygen atoms with an unpaired electron in a dangling sp^3 orbital. Previous studies have demonstrated that several variants of the E' centers, which exhibit subtle differences in their electron paramagnetic resonance (EPR) signals, exist in silica [5]. Although the microscopic structures of all these E' -center variants are not fully understood, the formation mechanism of the E'_1 center in α quartz, proposed originally by Feigl, Fowler, and Yip [6], is presently well accepted; that is, a positive hole, h^+ , trapped at a neutral oxygen monovacancy can be localized on one silicon atom and then lower its energy by relaxing back into the place of its three remaining oxygen neighbors. This reaction can be written as follows:



where \bullet and \equiv represent an unpaired electron and three $\text{Si}-\text{O}$ bonds, respectively. This model was subsequently refined by Rudra and Fowler [7], who suggested that the relaxation of the positively charged silicon is further stabilized by forming an additional $\text{Si}-\text{O}$ bond with a nearby oxygen atom, making the oxygen atom threefold coordinated [see Fig. 1(a)]. Since the E'_γ center, which is a fundamental paramagnetic center in $a\text{-SiO}_2$, exhibits similar EPR characteristics to the E'_1 center, it is commonly

believed that these two E' -center variants are essentially identical to each other [1–5]. To our knowledge, such an identification of the E'_γ center has not been seriously questioned for the past 25 years, and recent theoretical calculations appear to support the conjecture [8,9]. In this Letter, however, we propose that it seems to be natural *not* to assume that the E'_γ center in $a\text{-SiO}_2$ has the same

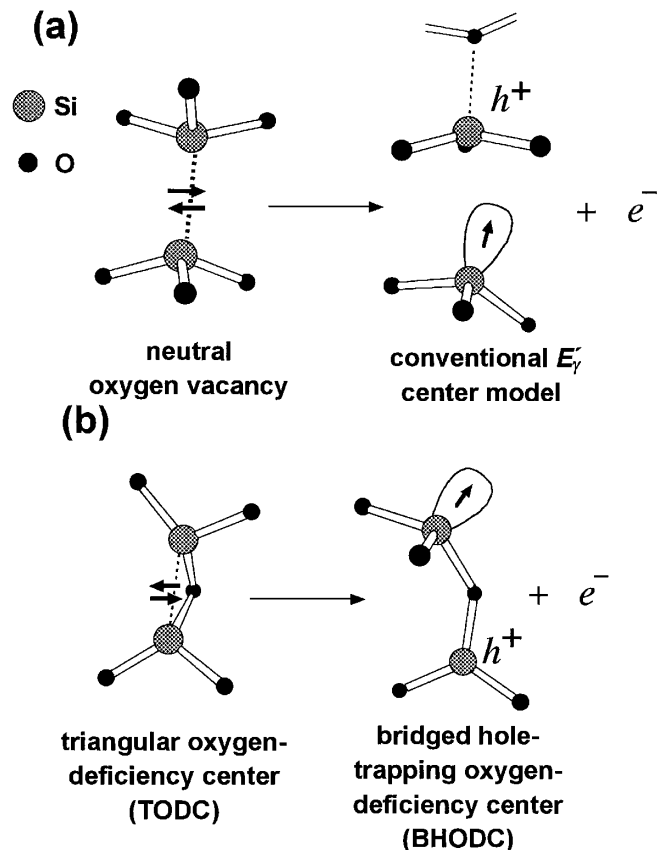


FIG. 1. (a) The conventional formation mechanism of the E'_γ center. (b) A new model of the E'_γ center (bridged hole-trapping oxygen-deficiency center, BHODC), in which a paramagnetic silicon shares a common oxygen with a neighboring hole-trapping silicon. One of the neutral precursors of BHODC consists of two three-coordinated silicon atoms, resulting in a triangular conformation called a triangular oxygen deficiency center (TODC).

microscopic origin as that of the E'_1 center in α -quartz. We then present an alternative model of the E'_γ center that may replace the conventional defect model of α -SiO₂.

Thus far, the Feigl-Fowler-Yip (FFY) model of the E'_1 center [6] has been tested by a number of theoretical approaches [7–12]. In particular, quantum-chemical calculations using clusters of atoms that model the local structure of the relevant defects have been extensively used to determine their electronic structures [7,9,11,12]. For cluster calculations of a perfect crystalline lattice [7,9,11,12], the initial position of the constituent atoms is taken from the corresponding crystal. To saturate the “surface” dangling bonds of the model cluster, hydrogen atoms are commonly used. The geometry of the cluster thus formed is fully optimized to obtain its minimum energy configuration. To create an oxygen vacancy, one of the oxygen atoms in the optimized cluster is then removed, and a further geometry optimization is carried out on the condition that only the inner O and Si atoms are allowed to relax. In other words, the position of the terminated H atoms are held fixed, which may be required to retain realistic configurations of the vacancy site in the corresponding crystalline lattice. Under these structural constraints, it has been shown that the proposed asymmetric relaxation of the hole trapped oxygen vacancy mentioned above indeed occurs [7,9,11,12], and the microscopic origins of the E'_1 center in α quartz along with the E'_γ center in α -SiO₂ have thus been interpreted.

However, do such structural constraints as derived from a crystalline lattice still hold in the case of the amorphous system as well? The E'_γ center in α -SiO₂ can be produced by ionizing radiations such as KrF or ArF excimer laser pulses, inducing macroscopic structural changes accompanied by matrix compaction [13,14]. These photoinduced structural changes are peculiar to amorphous solids and cannot be observed in the corresponding crystalline materials [15]. This suggests that the formation of radiation induced defects in α -SiO₂ require atomic rearrangements or relaxations not only at the defect site of interest but also in the second- and/or third-neighboring spheres around the defect. It is, hence, reasonable to assume that any artificial structural constraints should not be imposed for cluster calculations modeling the photoinduced defects in α -SiO₂ having a more flexible network than α quartz.

In this work, we, therefore, carried out quantum-chemical calculations on clusters of atoms with free H atoms to simulate an oxygen monovacancy embedded in the random silica network. A precursor cluster (model 1) used to generate an oxygen monovacancy is shown in Fig. 2(a). Model 1 is so constructed as to include five- and six-membered rings, since they are the most frequently found rings in the network topology of α -SiO₂ [16]. The geometry of model 1 was fully optimized at the density-functional theory (DFT) levels using the 6-31G(d) basis set [17]. For the present DFT calculations, we used the B3LYP exchange-correlation functional consisting of the Lee-Yang-Parr correlation functional [18] in conjunction

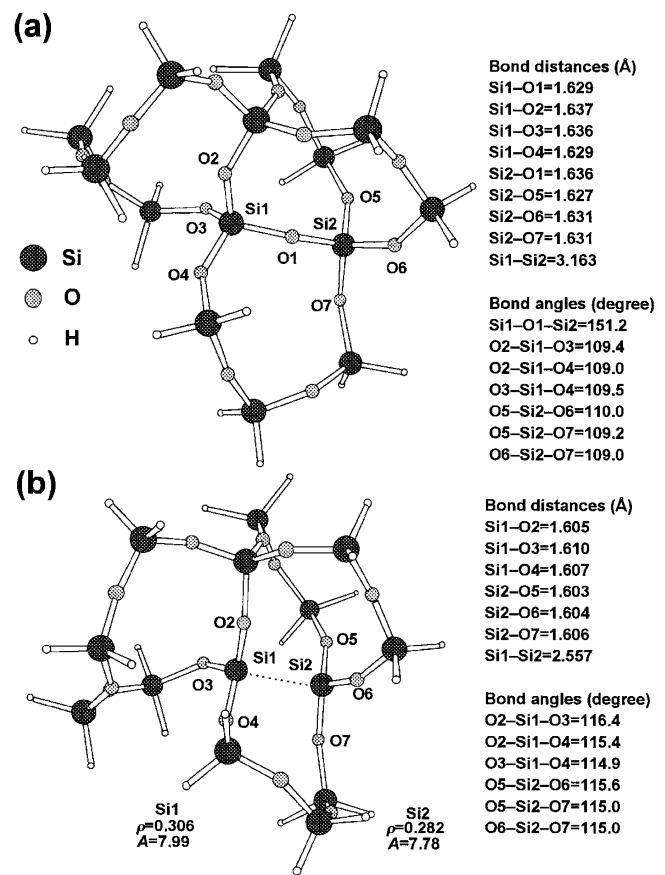


FIG. 2. Clusters of atoms modeling the local topology of amorphous silica: (a) a precursor cluster of an oxygen monovacancy ($\text{Si}_{14}\text{O}_{17}\text{H}_{22}$), model 1; (b) a charged oxygen monovacancy ($\text{Si}_{14}\text{O}_{16}\text{H}_{22}$)⁺, model 2. Principal bond distances (in Å), bond angles (in degrees), spin densities, ρ , and hyperfine coupling constants (in mT), A , are also shown. Geometry optimizations were performed at the B3LYP/6-31G(d) level.

with a hybrid exchange functional proposed by Becke [19]. A model of a charged oxygen monovacancy [model 2, see Fig. 2(b)] was then generated by removing one of the bridging oxygens (O1) in model 1, and its geometry was again fully optimized at the B3LYP/6-31G(d) level by assuming a total charge of +1. All the quantum-chemical calculations in this work were carried out with the GAUSSIAN98 program [20].

From these cluster calculations, it has been found that the asymmetric relaxation expected from the FFY model never occurs for model 2; on the contrary, as shown in Fig. 2(b), the unpaired electron is almost equally distributed over the two three-coordinated Si atoms [21]. The degree of localization of the unpaired spin can also be evaluated from the isotropic hyperfine coupling constant, A . In model 2, the two Si atoms in the defect site yield almost identical hyperfine couplings ($A \sim 8$ mT), and these values are far smaller than the experimental value observed for the E'_γ center in α -SiO₂ ($A = 42$ mT). It should also be worth mentioning that, even if we start from

several asymmetric configurations of the defect site in the optimizations, such a symmetric relaxation as shown in Fig. 2(b) occurs as well. These results strongly suggest that, at the charged oxygen monovacancy site in α -SiO₂, there exists only a single potential well that leads to a symmetric relaxation. It has recently been proposed by Chavez *et al.* [22] and Pacchioni *et al.* [9] that such a delocalized unpaired electron over two nearly equivalent Si atoms may explain the microscopic structure of another E' -center variant called the E'_δ center. These calculated results allow us to conclude that the structural model of the E'_1 center in α quartz may not be applicable to the E'_γ center in α -SiO₂ as is.

To shed new light on the microscopic origin of the E'_γ center, we then propose an alternative model of the hole trapped oxygen-vacancy center in α -SiO₂. This model consists of two types of three-coordinated silicons: one is paramagnetic and the other positively charged, similar to the case of the conventional FFY model. However, we assumed that these two types of silicon atoms can be bridged by a common oxygen atom, yielding a defect configuration shown in Fig. 1(b). We refer to this new type of defect as a “bridged hole-trapping oxygen-deficiency center (BHODC),” and one of its possible neutral precursors is called a “triangular oxygen-deficiency center (TODC)” [see also Fig. 1(b)]. Stefanov *et al.* [23] have recently reported that such a defect configuration as seen in TODC indeed exists at the Si-SiO₂ interface as an intermediate during silicon oxide formation (these authors call it a silicon epoxide). According to our preliminary calculations [24], the equilibrium geometry of BHODC can be obtained without imposing any structural constraints; that is, a true minimum geometry is attainable to BHODC, indicating that BHODC is more likely to exist in α -SiO₂ than the E'_1 -like defect. We [24] have shown that a complete symmetric form of the BHODC, in which the unpaired electron is equally distributed over two equivalent Si atoms in the defect, is higher in total energy by ~ 0.6 eV than the asymmetric BHODC. Furthermore, we have recently shown that the BHODC can originate not only from the TODC but from the divalent defect on ionizing irradiation [25]. These calculated results were obtained for model clusters having four to eight silicon atoms. To corroborate the validity of the BHODC model, in this work we perform further cluster calculations at the B3LYP/6-31G(d) level using a much larger cluster (model 3) having 14 silicon atoms. As shown in Fig. 3(a), model 3 is composed of five- and six-membered rings and, hence, can be regarded as a reasonable model of BHODC embedded in the network of α -SiO₂. In accordance with our preliminary calculations, we have obtained a minimum energy configuration for model 3. It has also been found that the hyperfine parameter calculated for the paramagnetic part of the defect ($A = 43.3$ mT) agrees well with the observed 42-mT splitting of the E'_γ center [26]. It is, hence, quite likely that our new model of the

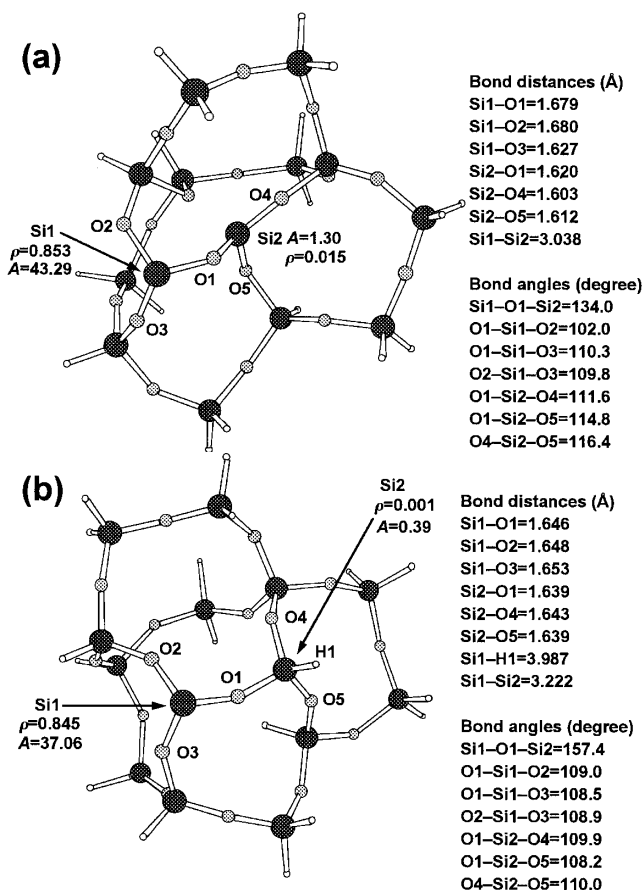


FIG. 3. Clusters of atoms modeling the local topology of amorphous silica: (a) BHODC, (Si₁₄O₁₈H₁₈)⁺, model 3; (b) a hydrogen associated center, Si₁₄O₁₈H₁₉, model 4. Principal bond distances (in Å), bond angles (in degrees), spin densities, ρ , and hyperfine coupling constants (in mT), A , are also shown. Geometry optimizations were performed at the B3LYP/6-31G(d) level.

charged paramagnetic center, BHODC, is a good candidate for the E'_γ center that is supposed to exist especially in α -SiO₂.

Moreover, we here show that BHODC is also capable of explaining the experimental feature of another E' -center variant, E'_β , whose structural origin still remains to be solved. It has previously been suggested that the oxygen monovacancy serves both as a precursor of the E'_β center and as a trapping site for atomic hydrogen, H⁰ [5]:



However, this reaction mechanism appears to be inconsistent with the EPR line shape of the E'_β center, which exhibits no hyperfine interaction with a proton and implies a large separation (~ 5 Å) between the proton and the unpaired spin [27]. In α quartz, however, such a large separation cannot be observed for the E' centers (E'_2 and E'_4) associated with hydrogen; the estimated distance between the nucleus of the hydrogen and the unpaired electron is ~ 1.5 (E'_4) and ~ 3 (E'_2) Å [28]. This means that, if Eq. (2) is valid, much longer range relaxations must occur in the

network of α -SiO₂ than that in α quartz. On the other hand, the BHODC model may not require such long range relaxations to fulfill a large separation between the proton and the spin. To elucidate the possibility, we added H⁰ to the defect site in model 3, and a full geometry optimization was performed for this cluster in the neutral charge state. As shown in Fig. 3(b), model 4 resulted in the configuration comprising the $\equiv\text{Si}\bullet$ and $\equiv\text{Si}-\text{H}$ units. The interatomic distance between the paramagnetic silicon and the newly added hydrogen atom is ~ 4.0 Å, which may account for the observed large separation between the unpaired spin and the proton. In addition, the calculated hyperfine coupling of the paramagnetic silicon in model 4 ($A = 37.1$ mT) is in reasonable agreement with the observed value for the E'_β center ($A = 42$ mT).

From the foregoing calculations and discussions, it is highly likely that, as for the point defects in α -SiO₂, the weight of the evidence is against the conventional E' -center model. We, therefore, suggest that this long-lasting model should now be replaced by our new model, BHODCs, which will give a new insight into the microscopic origins of fundamental paramagnetic defect centers in α -SiO₂.

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Note added in proof.—We have recently shown [29] that the present BHODC model can further account for the diffusion-limited anneal mechanism of the E' center to form the peroxy-radical defect in amorphous silica.

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